Oxidation of SiC/BN/SiC Composites in Reduced Oxygen Partial Pressures

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SiC fiber-reinforced SiC composites with a BN interphase are proposed for use as leading edge structures of hypersonic vehicles. The durability of these materials under hypersonic flight conditions is therefore of interest. Thermogravimetric analysis was used to characterize the oxidation kinetics of both the constituent fibers and composite coupons at four temperatures: 816, 1149, 1343, and 1538°C (1500, 2100, 2450, and 2800°F) and in oxygen partial pressures between 5% and 0.1% (balance argon) at 1 atm total pressure. One edge of the coupons was ground off so the effects of oxygen ingress into the composite could be monitored by post-test SEM and EDS. Additional characterization of the oxidation products was conducted by XPS and TOF-SIMS. Under most conditions, the BN oxidized rapidly, leading to the formation of borosilicate glass. Rapid initial oxidation followed by volatilization of boria lead to protective oxide formation and further oxidation was slow. At 1538C in 5% oxygen, both the fibers and coupons exhibited borosilicate glass formation and bubbling. At 1538C in 0.1% oxygen, active oxidation of both the fibers and the composites was observed leading to rapid SiC degradation. BN oxidation at 1538C in 0.1% oxygen was not significant.

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Motivation

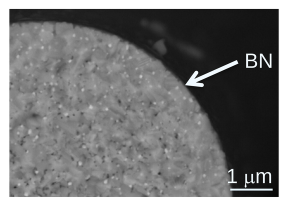
Technical challenge for hypersonic vehicles:
Develop lightweight, durable, reusable, 3000°F (1650°C) structurally-integrated Thermal Protection Systems (TPS) to carry both thermal and mechanical loads using ceramic matrix composite materials

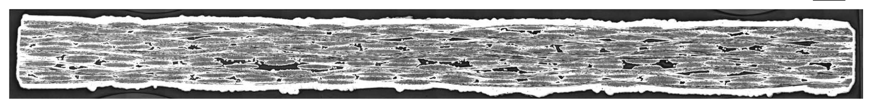
Objectives

- Characterize the oxidation resistance of BN-coated SiC fiber-reinforced SiC composites at temperatures and oxygen partial pressures relevant for hypersonic environments
- Develop understanding of oxidation degradation kinetics and mechanisms
- Provide data to Materials Research and Design, Inc. for incorporation in FEM for SiC/SiC degradation

Materials and Procedure

- Sylramic iBN fibers
  - Stoichiometric polycrystalline β-SiC
  - 3 wt% TiB_2, 1.3 wt % B_4C, 0.7 wt% BN
  - Heat treated in N_2 to form *in situ* BN surface layer (iBN), <100 nm
  - 800 fibers/tow, 6 tows/test
- SiC/BN/SiC composites
  - Sylramic iBN fibers
  - CVI Si-doped BN-coated fabric
  - CVI SiC matrix
- ThermoGravimetric Analysis (TGA)
  - 5% O_2/Ar or 0.1% O_2/Ar, 100 sccm (0.4 cm/sec)
  - 816, 1149, 1343, 1538°C (1500, 2100, 2450, 2800°F)
  - 100h maximum time, shorter times to investigate kinetics
- SEM, EDS, TOF-SIMS, XPS to characterize oxidation products





Possible reactions

Oxide formation

$SiC + 3/2\,O_2(g) = SiO_2 + CO(g)$

$2\,BN + 3/2\,O_2(g) = B_2O_3 + N_2(g)$

$SiO_2 + B_2O_3$ = borosilicate glass

Oxide volatilization

$B_2O_3 = B_2O_3(g)$

$B_2O_3 + ½\,O_2(g) = 2\,BO_2(g)$

$B_2O_3 + H_2O(g) = 2\,HBO_2(g)$

Active Oxidation

$SiC + O_2(g) = SiO(g) + CO(g)$

Summary and Conclusions

- Minimal oxidation of Sylramic iBN fibers or SiC/BN/SiC composites occurs at 816°C
- Transient borosilicate glass formation occurs at 1149 and 1343°C followed by boria volatility, leaving a protective silica scale on both fibers and composites
- Destructive oxidation of fibers and composites occurs at 1538°C
  - 5% O_2: excessive borosilicate glass formation, SiC fluxing, and glass bubble formation
  - 0.1% O_2: active oxidation of SiC to form SiO(g) observed

Acknowledgments

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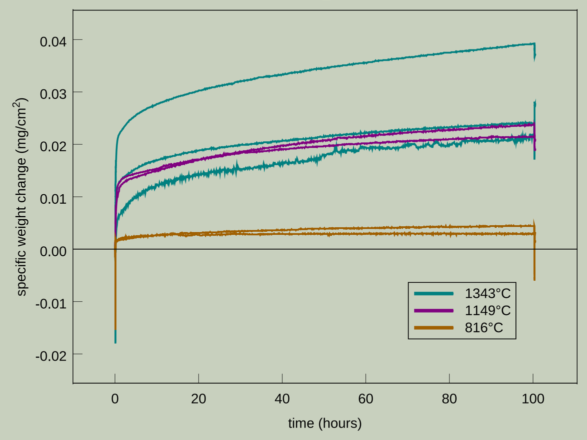
Fiber Oxidation

Oxidation weight change for Sylramic iBN fibers

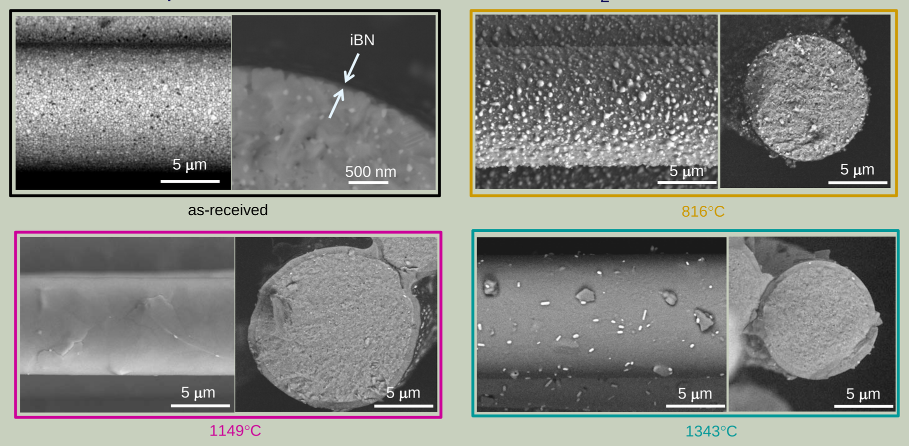
5% O_2/Ar



- Rapid transient weight gain followed by slow oxidation rate
- Variation in weight gain during transient phase at 1343°C
- Weight change at 1538°C not available due to extensive borosilicate bubble formation/interaction with furnace tube

Microstructure of oxidized fibers

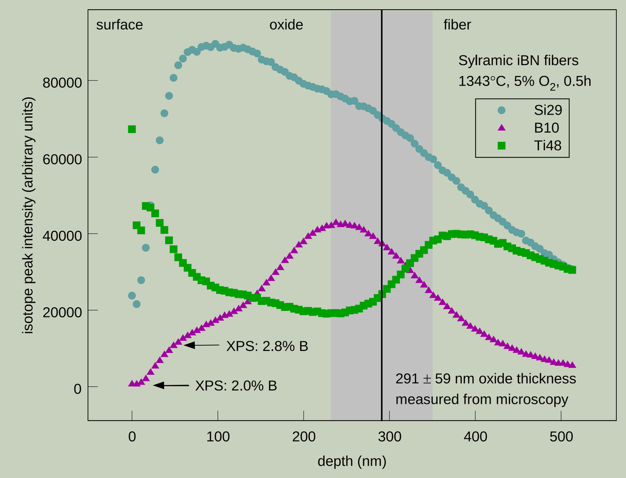
plan view and fracture sections, 5% O_2/Ar, 100 hr



Thickness of oxide scales consistent with weight change

TOF-SIMS and XPS analysis of oxide scale

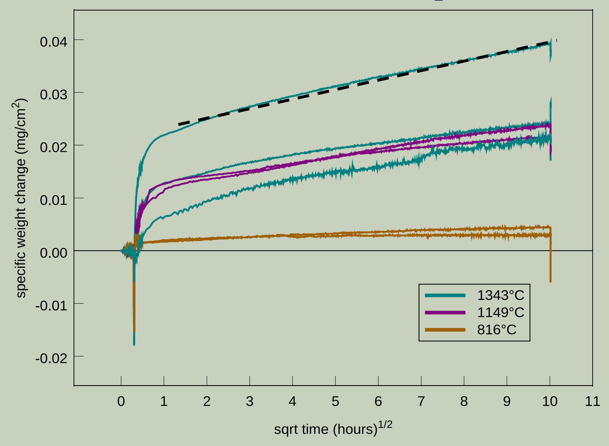
Sylramic iBN fibers



TOF-SIMS and XPS show boron gradient in oxide and boron depletion at surface.

"Parabolic" oxidation kinetics observed after transient

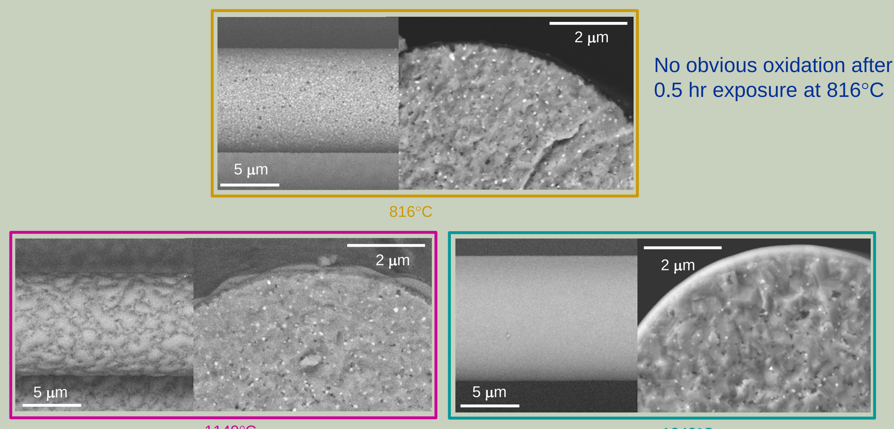
Sylramic iBN Fibers, 5% O_2/Ar



- Low rates and balance drift result in large uncertainty in measured slopes, rate constants
- Apparent parabolic rates are slower than those predicted for oxidation of pure SiC

Microstructure of oxidized fibers

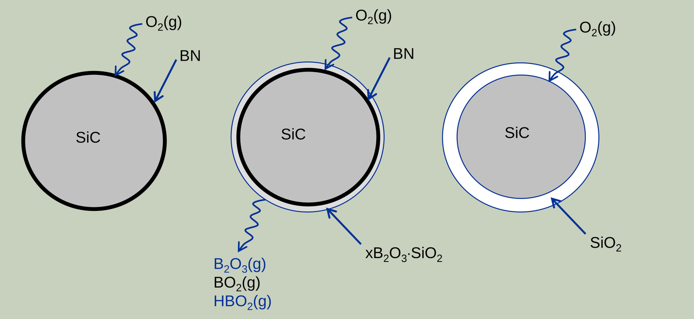
plan view and fracture sections, 5% O_2/Ar, 0.5 hr



No obvious oxidation after 0.5 hr exposure at 816°C

Thick oxide scales observed after oxidation at short times consistent with rapid transient weight change

Mechanism for oxidation of Sylramic iBN fibers



Oxygen reacts with BN forming B_2O_3, fluxing SiC.

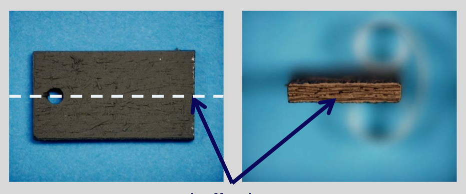
Borosilicate forms leading to rapid oxidation kinetics. Boron volatilizes from oxide surface.

BN is completely consumed by oxidation. Boron in glass is completely volatilized. Oxidation kinetics slow to those for pure SiC.

Coupon Oxidation

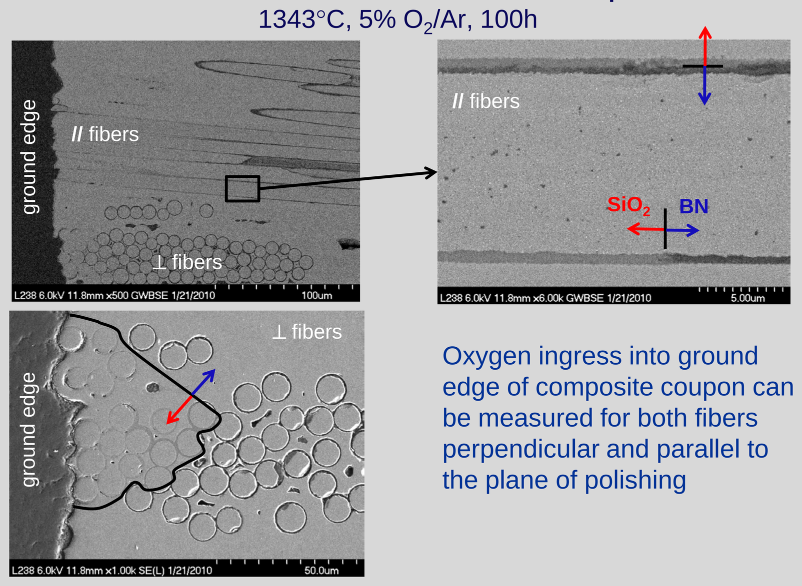
Oxidation of SiC/BN/SiC coupons

- Weight change for SiC/BN/SiC coupons (bottom edge of SiC seal coat ground off) is minimal under most conditions
- Coupons sectioned and distance of oxygen ingress, loss of BN from open edge determined by microscopy



Microstructure of Oxidized Coupons

1343°C, 5% O_2/Ar, 100h



Oxygen ingress into ground edge of composite coupon can be measured for both fibers perpendicular and parallel to the plane of polishing

Summary of SiC/BN/SiC composite oxidation

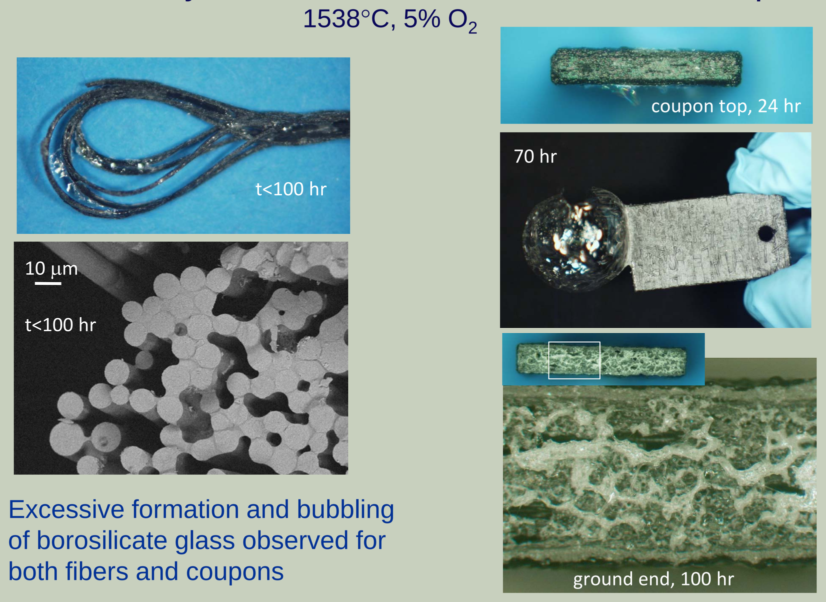
Temp., °C	orientation	5% O_2, 100 h	5% O_2, 24h	1000 ppm O_2, 100 h	1000 ppm O2, 24h
1538	// fibers	1 fiber diameter (n=6) thick scale on edge	Intermittent BN/SiO_2	Active oxidation of SiC and borosilicate bubbling	Active oxidation of SiC, minimal SiO_2, no loss of BN
	⊥ fibers	46±30 μm (n=12)			
1343	// fibers	119±24 μm (n=13)	61±32 μm (n=22)	15±8 μm (n=16)	Intermittent SiO_2 38 μm (n=8) Continuous SiO_2 16±4 μm (n=8)
	⊥ fibers	3 fiber diameters	2 fiber diameters	1 to 2 fiber diameters	Intermittent SiO_2, 2-3 fiber diameters (n=12)
1149	// fibers	2.8±3.1 μm (n=16)	3.8±2.1 μm (n=35)	Intermittent SiO_2 72±14 μm (n=16)	Intermittent SiO_2 0-38 μm (n=9)
	⊥ fibers	<1 fiber diameter	<1 fiber diameter	Intermittent SiO_2 4 fiber diameters (n=17)	Intermittent SiO_2, 1-2 fiber diameters (n=2/12)
816	// fibers	0.3 μm (n=2), 5 μm (n=1)	2 μm (n=3)	14 μm (n=2)	no oxidation visible
	⊥ fibers	<1 fiber diameter	<1 fiber diameter	1 fiber diameter	no oxidation visible

- Red = depth of SiO_2 formed, BN consumed, measured from ground edge
- Blue = depth of BN consumed without SiO_2 sealing edge, measured from ground edge
- Green = active oxidation of SiC to form SiO(g)
- n= number of observations

Oxidation at 1538°C

Oxidation of Sylramic iBN Fibers, SiC/BN/SiC coupons

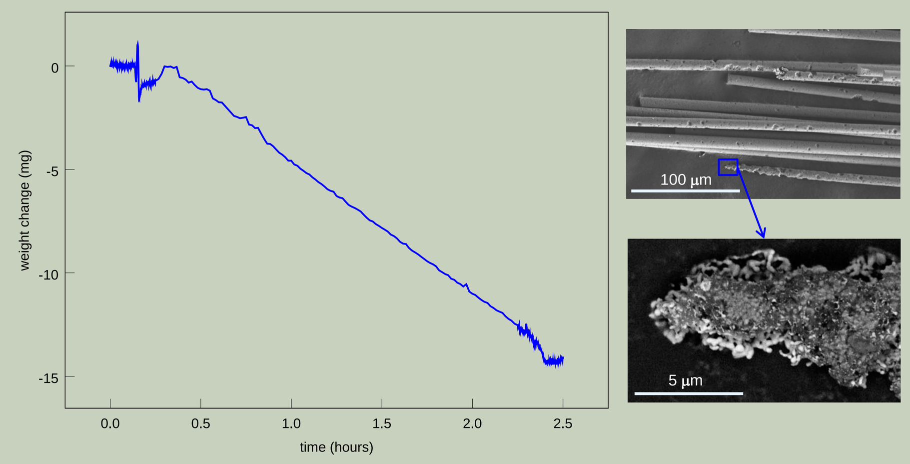
1538°C, 5% O_2



Excessive formation and bubbling of borosilicate glass observed for both fibers and coupons

Active oxidation of Sylramic iBN Fibers

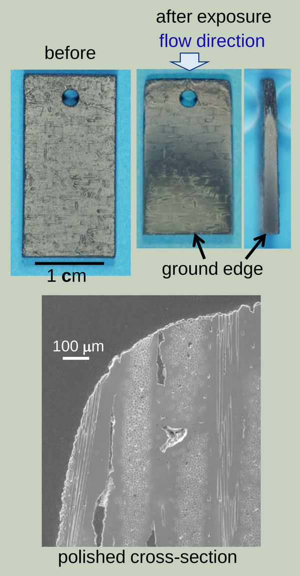
1538°C, 0.1% O_2

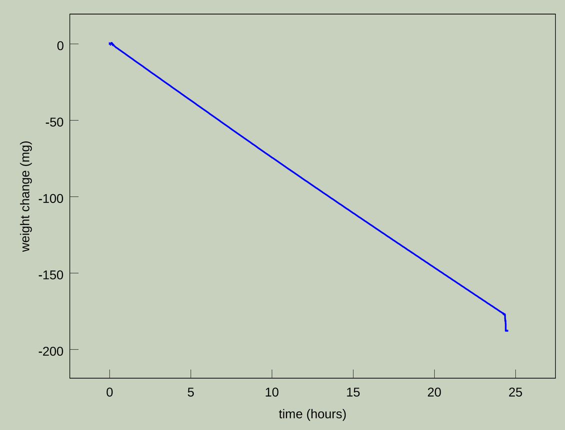


Rapid weight loss and degradation of fibers observed due to active oxidation of SiC to form SiO(g).

Active oxidation of SiC/BN/SiC coupons

1538°C, 0.1% O_2, 24h





loss of SiC seal coat observed due to active oxidation of SiC to form SiO(g).